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**EXPLORING THE KINETICS OF THE WATER-GAS SHIFT
REACTION ON INCONEL®600: A PROOF-OF-CONCEPT TEST**

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Introduction

Previous work done at the National Energy Technology Laboratory, NETL, on the kinetics of the high-temperature ($>700^{\circ}\text{C}$), high-pressure (16 atm), water-gas shift reaction (WGSR), found that the gas-phase reaction is greatly enhanced in the presence of Inconel®600, a high-performance alloy (Bustamante et al., 2004). Equilibrium conversions were attained at temperatures as low as 750°C when the reaction was carried out in a reactor made out of Inconel® 600. Preliminary characterization of the material after reaction showed changes in the surface chemistry suggesting a catalytic effect. Because the work at NETL was directed primarily toward the hydrogen-selective membrane reactor concept, no further attempts to correlate the catalytic effect on the reaction rate or to thoroughly examine changes in the properties of the Inconel®600 surfaces were performed. It is well known that many industrial applications deal with high-temperature, high-pressure streams where the water-gas shift reaction might have a large impact and, as a consequence, knowledge of the extent of the water-gas shift reaction on common construction materials is desirable.

The objective of this test was to determine whether the Hydrogen Membrane Test units, [HMTs], at NETL would be suitable for the high-temperature, high-pressure kinetic study of the heterogeneous catalytic effects of common construction materials. The test would be considered successful if small conversions, i.e. less than 10%, can be accurately calculated.

Experimental

For the proof-of-concept test it was decided to pack a quartz reactor with a mixture of quartz and Inconel®600 packing. Details of the packing of the reactor, estimation of the surface area, and conditions used in the test will be given after a short description of the HMT unit.

Figure 1 provides a schematic representation of HMT. The reaction temperature was controlled with a ceramic resistance heater using a control loop with a coaxially mounted, dual element type-K thermocouple (TI), which was placed approximately 3 mm from the reactor. The reaction pressure was controlled with a stainless steel Badger Research pressure control valve (PCV) employing a control loop with a pressure indicator (PI). De-ionized liquid water, pumped by an ISCO 500D pump, was injected into the gas stream through a 0.10 mm ID tubing. The gas stream was constituted by carbon monoxide, carbon dioxide and hydrogen. The flowrate of each gas was controlled with Brooks 5850i mass flow controllers. The tubing upstream of the reactor was heated-up to about 200°C to effect the evaporation of the injected liquid water droplets into the gas stream. Unlike previous experiments at NETL, a trap was placed downstream of the reactor to facilitate the handling of high concentrations of water at high-pressure because tubing downstream

of the reactor could not be heated to the temperature required to prevent the condensation of water due to the presence of the pressure-control valve.

An oxygen trap was located in the gas mixture inlet line to eliminate the pronounced catalytic influence of O₂ on the reaction. Argon was continually bubbled in the water reservoir to prevent diffusion of air into the water stream.

The pressure drop across the reactor wall was minimized by admitting part of the inlet gas mixture into the annular space between the containment tube (38 mm, Inconel®600) and the quartz reactor. This ‘pressure equalization mixture’ is stagnant and would be expected to reach equilibrium conversion, i.e. there would be a gradient of concentration between the feed stream and the stagnant zone. It was found that back-diffusion into the main feed line was negligible.

Figure 2 depicts the empty quartz reactor. Computational Fluid Dynamic [CFD] modeling demonstrated that the empty reactor behaves like a laminar flow reactor, with small deviations from the ideal behavior, i.e. the average residence time was slightly lower than that expected from a tubular flow reactor. Dimensions of the packed reactor are indicated in Table 1. The volume of the annular space, providing the rapid heat-up of the reactants from 600°C to the reaction temperature, was less than one-tenth of the reactor volume; no detectable reactant conversion occurred in that zone. (Control experiments with the quartz reactor had no detectable level of conversion at temperature lower than 700°C.)

The quartz reactor was filled with quartz and Inconel®600 packing. Small cylinders —of length, 3.5 or 4.2 mm and 2mm diameter— of Inconel®600 and quartz, respectively, were made from solid rods (2 mm diameter) of those materials. A total of 13 Inconel®600 pellets, amounting to a surface area of 3 cm², were added to the reactor. This surface area was selected so that conversions remained below 10% at the desired flowrate. Although this surface area target was based on extrapolation from the conversions obtained in previous experiments with a quartz-packed, Inconel®600 reactor (Inconel®600 surface area, 18cm²), the validity of the assumption was confirmed experimentally. Specifically, if conversions exceeded the target, an increase in the flowrate, i.e. a decrease in residence time, would have been made. Conversion could be increased by decreasing flowrate. An additional 47 quartz cylinders were added to ensure a homogeneous distribution of the packing throughout the volume of the reactor. The presence of quartz, assumed to be relatively inert for the water-gas shift reaction, would diminish the influence of mass-transfer limitations without affecting the kinetics on the Inconel®600. Figure 3 shows the reactor before testing.

A GC (HP-5890 II) equipped with a TCD detector was used to quantify all of the components of the reactor effluent. A porous polymer (HaySep® D) was used as column packing and helium was employed as the carrier gas. The high flowrate used in the test, which was significantly larger than the flowrate used in the calibration of the GC, produced artificially higher concentrations for each component, i.e. readings for the total concentration commonly exceeded 100%. However, tests performed with the calibration-

gas mixture showed that the response to high flowrates was the same for all components. Therefore, molar fractions calculated from the GC output were used in determining the conversions.

TABLE 1. Reactor dimensions.

Quartz ID, cm	1.1
Nipple length, cm	1.75
Distance between nipple and top of reactor, cm	0.64
Volume of Quartz packing, cm ³	0.62
Volume of Inconel®600 packing, cm ³	0.17
Reactor volume (empty), cm ³	2.22
Reactor volume (packed), cm ³	1.43

Procedure

The reactor was heated to 900°C in a flow of low-pressure (ambient) helium. A H₂O/He gas mixture was fed to the reactor in order to test the effectiveness of the water trap. It was found that most of the water was collected by the trap: only minor amounts were detected in the GC. Moreover, the amount of water in the trap was in excellent agreement with the amount of liquid water fed to the system.

A CO/CO₂/H₂O/H₂ gas mixture was then fed to the reactor. This first test was conducted at ambient pressure and 900°C. Residence time (defined on the basis of the available gas-phase volume, i.e. total volume minus packing volume) was very low, less than 0.05 s. Consequently, conversions were negligible; only a small amount of methane, about 0.01%, was detected. This experiment was intended to provide a base line to calculate conversions at higher residence times: the current reactor system lacks a by-pass and allows only the quantification of the outlet composition (which differs from the inlet composition whenever significant conversions are attained). The normalized gas composition observed in the low-pressure, low-residence time system is summarized in Table 2.

Table 2. Normalized inlet gas composition – Ambient pressure, 900°C.

Component	Composition (mole %)
H ₂	52.3
CO	23.2
CO ₂	1.1
H ₂ O	23.4

The high-temperature kinetic test was first conducted at 220 psig (~16 atm) in order to test a condition similar to previous kinetic studies carried out with empty quartz reactors at NETL. Data on the outlet composition and flowrates were collected after steady-state was attained. A total flowrate of 480 sccm was fed to the system, corresponding to a residence time of 0.6 s. Next, reactor pressure was increased to 400 psig (~28 atm) and the total flowrate was incremented to 820 sccm. The residence time and composition of

the gas mixture was expected to be similar to that observed during the test carried out at 220 psig. However, in going to high pressures (~28 atm) it was observed that a very small actuation of the pressure control valve, even to compensate for deviations from the set point as low as 1 psig, would cause a noticeable change in the flowrate downstream of the reactor (see Figure 4). Because it was not possible to fine tune the control system at this time, many data points were collected at each condition to obtain an average that would correctly represent the kinetic behavior of the system. Likewise, the base line composition determined at ambient pressure was not deemed appropriate for comparison with the high-pressure experiments. A two-fold approach was implemented to deal with this situation. Firstly, CO₂ was removed from the inlet gas mixture; any CO₂ observed downstream the reactor would be produced via the WGSR, providing an ‘internal standard’ to determine the conversion. Secondly, a new base-line test was conceived: the pressure inside the reactor would be kept at 28 atm while the reactor temperature is decreased to 500°C; this would match exactly the conditions in the kinetic test while giving negligible conversions. This experiment was scheduled for the end of the testing period.

Data were collected at 900, 850 and 800°C (400 psig) for the gas mixture with, and without, CO₂. A final test at 900°C and 400 psig, intended to determine whether there would be any change in the behavior of the Inconel®600 packing with time on stream, could not be carried out because of reactor failure. Levels of methane and carbon dioxide increased substantially and this could only be explained if the stagnant gas located between the Inconel® wall (of the containment tube) and the quartz reactor, i.e. the pressure equalization fluid, were diffusing into the quartz reactor. The unit was cooled down under inert gas and the quartz reactor was confirmed to be broken. Figure 5 is a photograph of the reactor.

Finally, the reactor was bypassed and the base line for the high-pressure reaction was determined by admitting the same amounts of CO, CO₂, H₂ and H₂O than in the actual reaction test. Conversions were calculated based on the molar flowrates so determined.

Results

Table 3 shows the conversions obtained for the CO/H₂/H₂O mixture; expected gas-phase conversions for the same residence time, inlet concentrations and temperature are given as comparison. Although the entries are sorted sequentially, it is important to bear in mind that this test was performed in the midst of the overall test: at a given temperature the CO₂ stream would be turned off and CO/H₂/H₂O would flow to the reactor. Conversions were evaluated from the outlet CO and CO₂ concentrations after steady state was reached, Equation 1. Conversions calculated in this way do not require a base line, obviating part of the problem introduced by the fluctuation of the PCV.

$$\text{Conversion, CO} = \frac{C_{CO_2, \text{outlet}}}{C_{CO, \text{outlet}} + C_{CO_2, \text{outlet}}} * 100 \quad (\text{Eq. 1})$$

Conversions in the Inconel-packed reactor are larger than the expected gas-phase conversions which clearly points to a catalytic effect due to the Inconel (quartz packing is inert at the temperatures studied). The results follow the expected trend of decreasing conversions with decreasing pressure. A large number of readings was taken at each condition to minimize the impact of the intrinsic variability of the system; the error was determined as the standard deviation divided by the average.

Table 3. CO conversions in the CO/H₂/H₂O mixture. All experiments carried out at the same residence time (~ 0.6 s).

Temperature (°C)	Pressure (psig)	Conversion (%)	Error (%)	Gas-phase conversion (%)
850	400	0.77	2.0	0.011
900	400	1.20	1.7	0.035
800	400	0.62	2.3	0.003

For determining the conversions in the CO/CO₂/H₂/H₂O mixture, the reactor was bypassed so that the inlet molar flowrates for CO and CO₂ could be determined from the inlet molar fractions and total flowrate. Conversions were then calculated by using Equation 2.

$$Conversion = \frac{MolarFlowrate_{Bypass} - MolarFlowrate_{Outlet}}{MolarFlowrate_{Bypass}} * 100 \quad (Eq. 2)$$

Table 4 summarizes the CO conversions at different temperatures and pressures; predicted gas-phase conversions are given for comparison¹. Each data set represents the average of the results obtained at those conditions. Repeated entries correspond to the same condition tested at different times.

Table 4. CO conversions in the CO/CO₂/H₂/H₂O mixture. All experiments carried out at the same residence time (~ 0.6 s).

Sequential Condition	Temperature (°C)	Pressure (psig)	Conversion (%)	Error (%)	Gas-phase conversion (%)
1	900	220	1.38	4.9	0.014
2	900	400	2.80	5.6	0.035
3	850	400	2.36	6.6	0.011
4	850	400	2.81	26.6	0.011
5	850	400	0.85	35.0	0.011
6	800	400	3.16	25.7	0.003

Even though the temperature and residence time are the same in conditions (1) and (2), conversions in the latter are larger as a consequence of the larger inlet concentrations at higher pressures. A decrease in temperature (2 to 3) leads to a decrease in conversion, as

¹ The effect of the opposite reaction (CO₂ + H₂) was neglected in the calculation.

expected. However, conversions at 850°C (4) surpass the conversions at 900°C (2). This could be related to the fact that between conditions (3) and (4) hydrogen was not fed into the system (the H₂ bottle was depleted during an inactive period). The absence of hydrogen would have increased the likelihood of deposition of carbon on the reactor. Interestingly, upon restoring the flow of hydrogen, large concentrations of methane (~0.3 %) were observed for a several hours, after which the amount diminished to the levels previously observed. The possibility of conditioning of the metallic surface by the gas stream is further suggested by the lower conversion displayed in entry (5). This condition was tested after the H₂/CO/H₂O test. Finally, the large conversions observed at 800°C and 400 psig (6) may have been the first indication of a leak in the reactor; shortly thereafter concentrations of CO₂ and methane increased ostensibly. After shutting down, the reactor was found to be broken.

Figure 5a is a picture of the reaction zone after reaction, while figure 5b shows both the reaction and heating zones. The leak is not shown in the picture. Unfortunately, it is not possible to determine whether the noticeable deposition of carbon inside the reactor, and perhaps on the Inconel®600 pellets, took place before or after damage to the reactor. The reaction was continued for a couple of days until it was clear that the strange behavior was not related to the operation of the system.

Formation of methane was clearly perceived throughout the duration of the test. However, the amounts were significantly lower than any other component. Additionally, an enhancement of the reaction rate with time on stream was appreciated for some specific conditions. However, due to the scatter of the data a trend could not be clearly established.

Conclusions

The high-temperature, high-pressure (~28 atm) WGSR was conducted in a quartz reactor packed with Inconel®600 and quartz packing. Conversions were calculated in the temperature range of 800-900°C, both for CO/CO₂/H₂/H₂O and CO/H₂/H₂O mixtures. Residence time was selected to minimize the gas-phase conversions.

Several operational problems were detected during the test. Firstly, it was not possible to fine-tune the reactor pressure controller. This would lead to periodic oscillations of the gas flowrate downstream from the reactor. Secondly, an accurate determination of the inlet composition was not possible. Both situations were dealt with and the data presented in this report is considered to be a good representation of the expected kinetics. However, a more definite solution ought to be pursued in future tests of this kind. Specifically, the use of certified, or custom-made, gas mixtures would allow for the direct evaluation of the conversions. Additionally, the existing infrastructure should be optimized with the implementation of a better cascade control model. Nevertheless, the existing infrastructure appears to be appropriate for the study of the reaction in a moderate-high pressure range, i.e. ~16 atm.

The catalytic effect of the Inconel®600 packing was confirmed. It was proven that conversions in the ‘kinetically-relevant’ range (i.e., small enough to prevent the opposing reaction —less than 10%— and large enough to be accurately measured) can be seen with the HMT. It is expected that with the implementation of the simple measures outlined above, the conversion data will have sufficient accuracy to be used in the evaluation of the kinetic parameters of the reaction.

Conversions evaluated from CO/CO₂/H₂/H₂O and CO/H₂/H₂O mixtures differed. It is expected that the accuracy of the former data is less due to the additional fluctuations introduced by addition of relatively small amounts of CO₂.

Formation of methane was observed throughout the test but the extent of the methane-forming reactions appears to be significantly lower than the extent of the WGSR.

References

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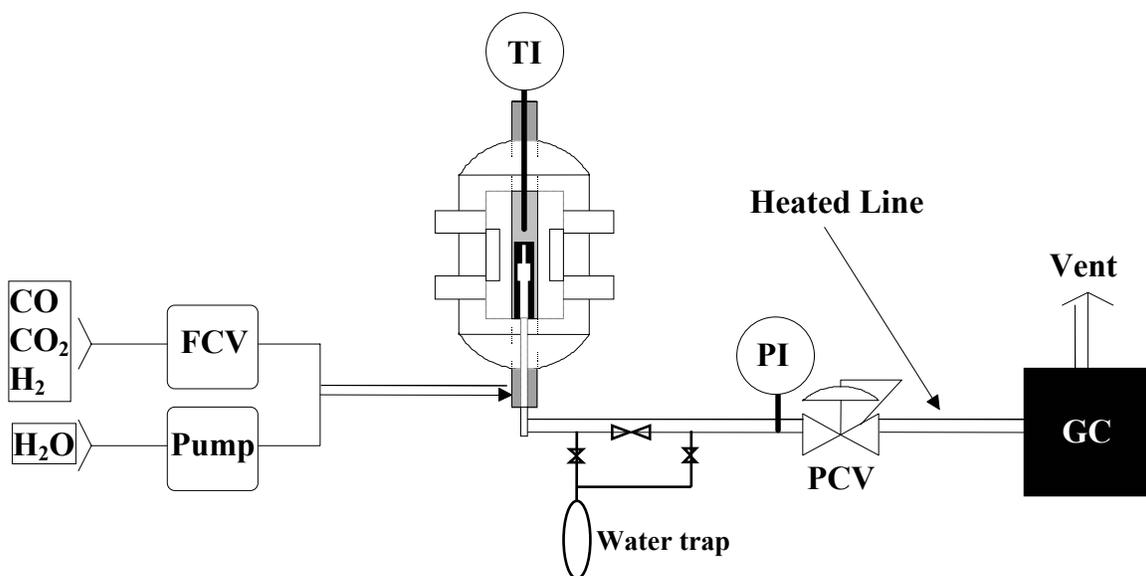


Figure 1. Overview of the HMT unit.

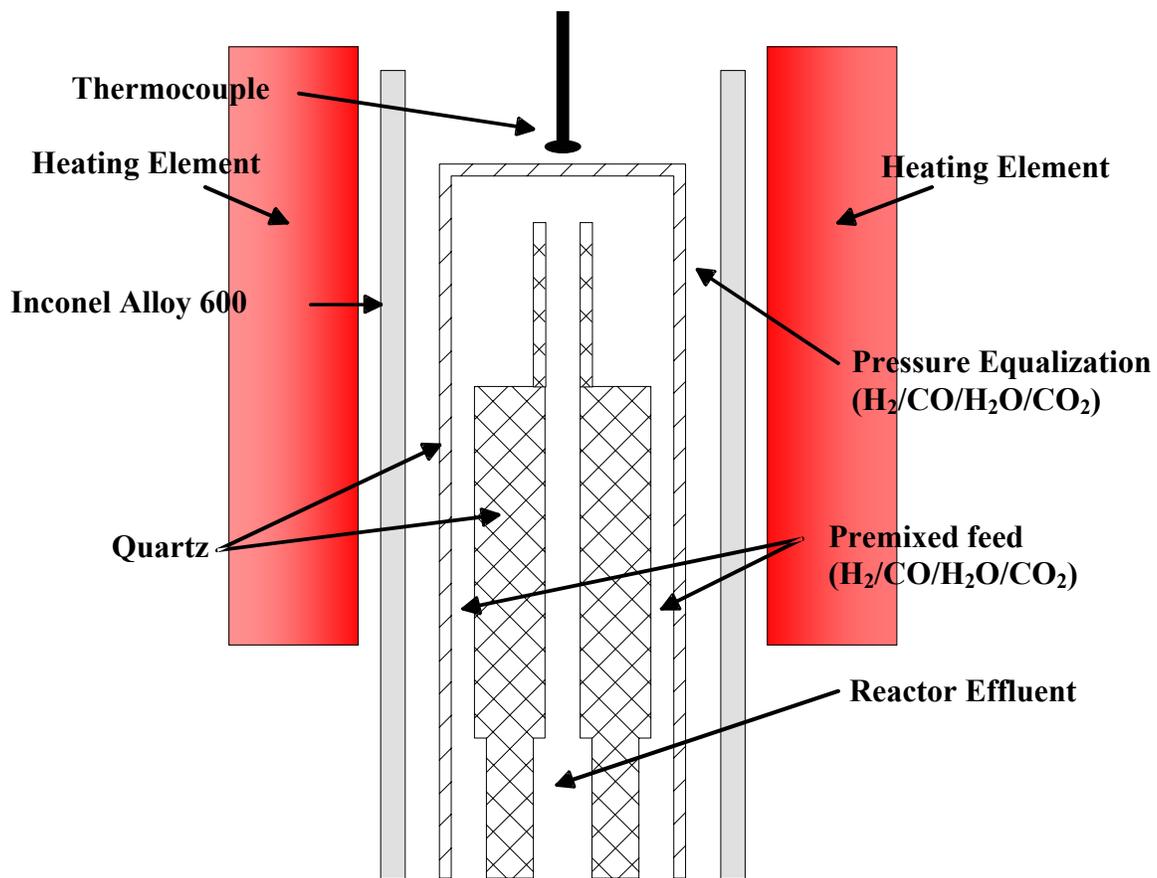


Figure 2. Schematic of the empty quartz reactor.



Figure 3. Quartz reactor packed with Inconel®600 and quartz packing.

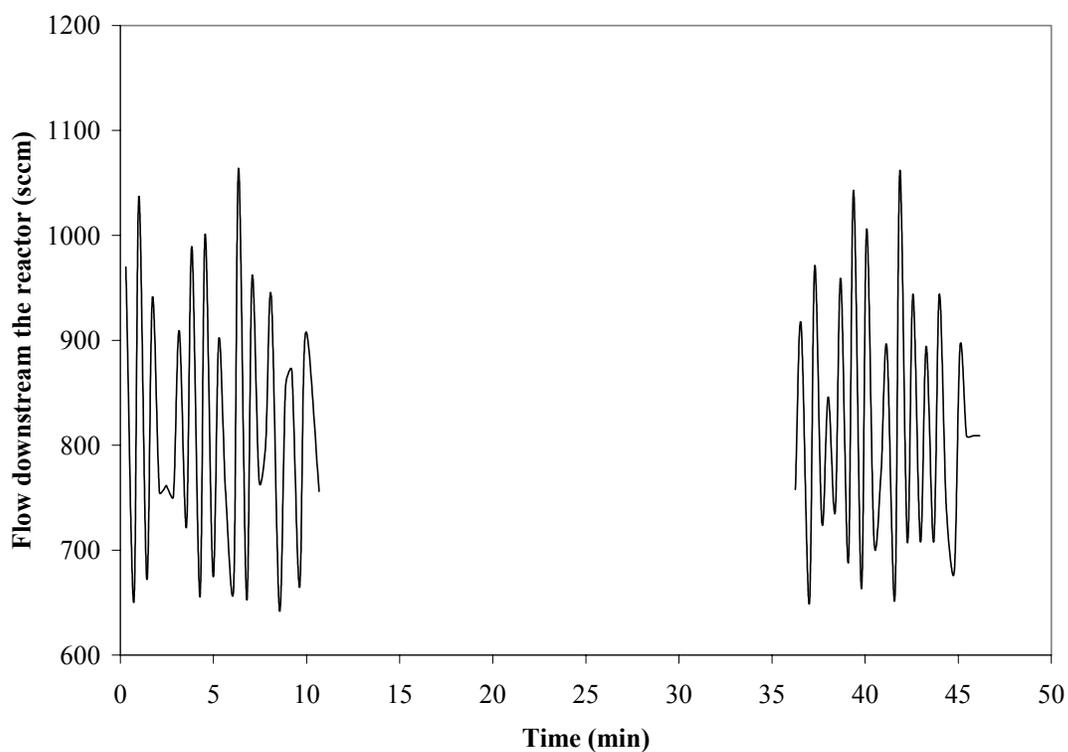


Figure 4. Fluctuations in the flowrate downstream from the reactor, resulting from very small actuations of the PCV. Note that the average flowrate is constant.

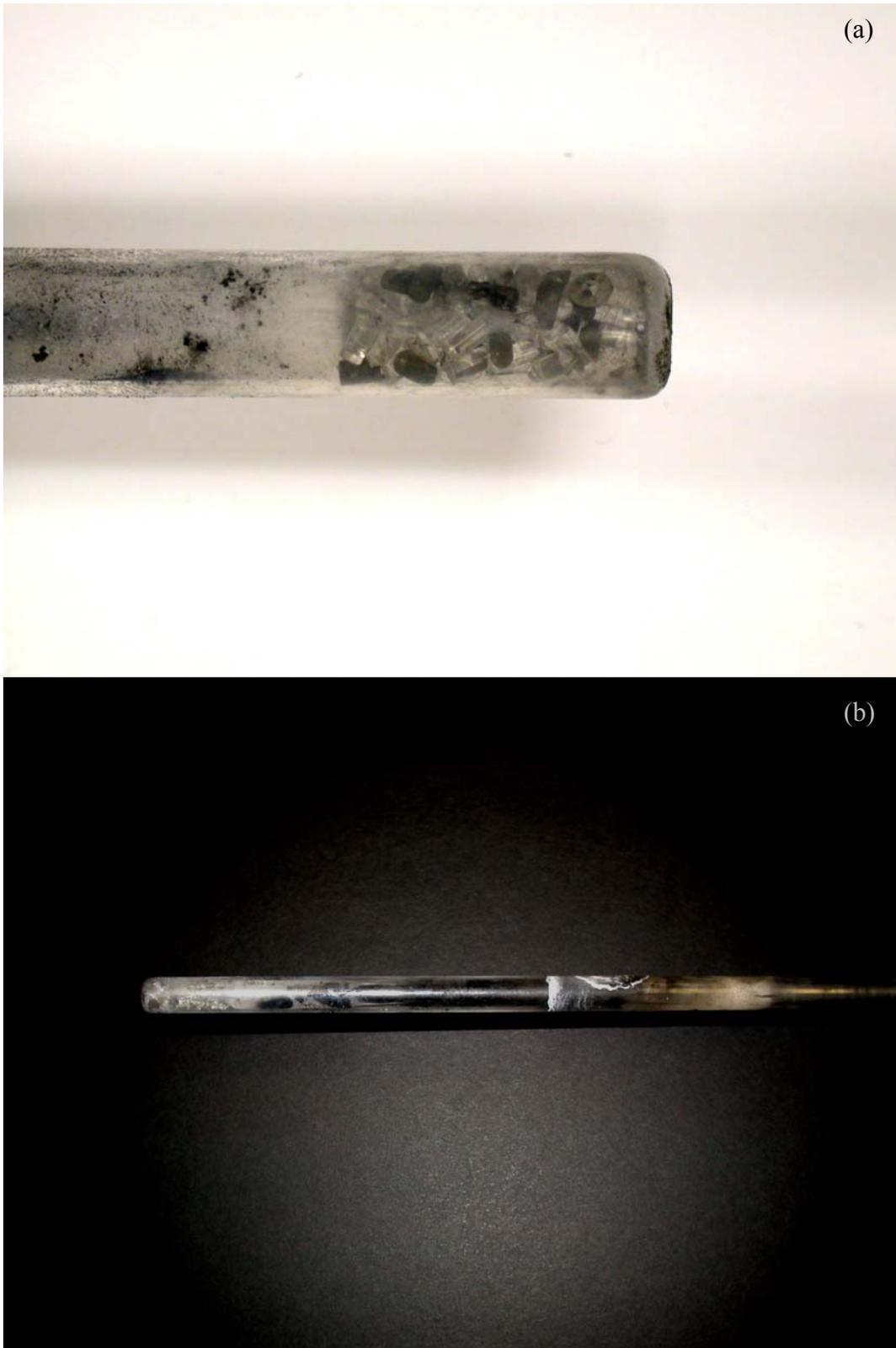


Figure 5. Reactor after reaction: a) Reaction zone, b) Reaction zone and preheating section.